

THE ELECTRON-GAS PAIR DENSITIES AND THEIR NORMALIZATION SUM RULES IN TERMS OF OVERHAUSER GEMINALS AND CORRESPONDING SCATTERING PHASE SHIFTS

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It is shown, how the normalization sum rules of the spin-parallel and spin-antiparallel pair densities of the homogeneous electron gas become sum rules for the scattering phase shifts of the Overhauser two-body wave functions (geminals), with which the pair densities have been successfully parametrized recently. These new sum rules relate two-body quantities to a one-body quantity, namely the asymptotics of the Overhauser geminals to the momentum distribution.

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The (spin-unpolarized) homogeneous electron gas (HEG) is an important and widely used model for the phenomenon called electron correlation, cf. e.g.¹. Some of its details are hidden in the reduced densities. For the HEG ground state such characteristic quantum-kinematic quantities are (i) the momentum distribution $n(k)$ as the typical 1-body quantity (recently parametrized in terms of a special convex function²) and (ii) the pair density (PD) $g(r)$ as the typical 2-body quantity (recently parametrized in Refs.³⁻⁵). With spin-resolution one has to distinguish the PDs $g_{\uparrow\uparrow}(r)$ and $g_{\uparrow\downarrow}(r)$ for electron pairs with an interelectron distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and with parallel and antiparallel spins, respectively. They describe the probabilities of finding in the neighborhood of an electron (the ‘blue’ electron) another electron with the same respectively the opposite spin. So it holds $g_{\uparrow\uparrow}(r) \geq 0$ and $g_{\uparrow\downarrow}(r) \geq 0$. For large r it is $g_{\uparrow\uparrow}(\infty) = 1$ and $g_{\uparrow\downarrow}(\infty) = 1$. For $r = 0$ (‘on-top’) it is $g_{\uparrow\uparrow}(0) = 0$ due to the Pauli repulsion and $g_{\uparrow\downarrow}(0) < 1$ due to the Coulomb repulsion. These short-range deviations of $g_{\uparrow\uparrow}(r)$ and $g_{\uparrow\downarrow}(r)$ from their asymptotical values 1 are called Fermi hole and Coulomb hole, respectively. In between they show shell structures. They are normalized as (cf. e.g.⁶)

$$\rho \int d^3r [1 - g_{\uparrow\uparrow}(r)] = 2, \quad \rho \int d^3r [1 - g_{\uparrow\downarrow}(r)] = 0 \quad (1)$$

with ρ = electron density. The spin-summed PD $g(r) = \frac{1}{2}[g_{\uparrow\uparrow}(r) + g_{\uparrow\downarrow}(r)]$ is therefore normalized as $\rho \int d^3r [1 - g(r)] = 1$, what is called perfect screening sum rule or charge neutrality condition. Here and in the following wave lengths and momenta k are measured in units of the Fermi wave length $k_F = \frac{1}{\alpha r_s}$, $\alpha = (\frac{4}{9\pi})^{1/3}$ and lengths (like r or $\rho^{-1/3}$) in units of k_F^{-1} . Therefore $\rho = \frac{1}{3\pi^2}$ and $\rho d^3r = \alpha^3 d(r^3)$. The momentum distribution and the PDs depend parametrically on r_s , the radius of a sphere containing in the average one electron, measuring simultaneously the interaction strength with $r_s = 0$ corresponding to the ideal Fermi gas. In Refs.³⁻⁵ the PDs as functions of the separation r and of the parameter r_s have

been fitted to the data of quantum Monte-Carlo calculations. With the help of (such available) PDs, particle-number fluctuations in fragments of the system can be discussed.⁷ The partitioning into a generalized Hartree-Fock term and a connected remainder

$$\begin{aligned} g_{\uparrow\uparrow}(r) &= g_{\uparrow\uparrow}^{\text{HF}}(r) - h_{\uparrow\uparrow}(r), & g_{\uparrow\uparrow}^{\text{HF}}(r) &= 1 - |f(r)|^2, \\ g_{\uparrow\downarrow}(r) &= g_{\uparrow\downarrow}^{\text{HF}}(r) - h_{\uparrow\downarrow}(r), & g_{\uparrow\downarrow}^{\text{HF}}(r) &= 1 \end{aligned} \quad (2)$$

defines the cumulant PDs $h_{\uparrow\uparrow}(r)$ and $h_{\uparrow\downarrow}(r)$. $f(r) = (2/N) \sum_{\mathbf{k}} n(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}}$ is the dimensionless 1-body reduced density matrix. $f(0) = 1$ expresses the normalization of $n(k)$. The hole normalizations (1) imply

$$\rho \int d^3r h_{\uparrow\uparrow}(r) = 2c, \quad \rho \int d^3r h_{\uparrow\downarrow}(r) = 0, \quad (3)$$

where $c = (2/N) \sum_{\mathbf{k}} n(\mathbf{k})[1 - n(\mathbf{k})]$ is christened Löwdin parameter⁸ (measuring the correlation induced nonidem-potency of $n(k)$, thus vanishing for $n(k) \rightarrow n^{(0)} = \Theta(1 - k)$). It is easy to show that

$$g_{\uparrow\uparrow}^{\text{HF}}(r) = 2g_-(r), \quad g_{\uparrow\downarrow}^{\text{HF}}(r) = g_+(r) + g_-(r), \quad (4)$$

define a singlet term $g_+^{\text{HF}}(r)$ and a triplet term $g_-^{\text{HF}}(r)$ with

$$g_{\pm}^{\text{HF}}(r) = \sum_L^{\pm} \langle j_L^2(kr) \rangle, \quad L = (l, m_l), \quad (5)$$

where \pm refer to even and odd l , respectively, and $\sum_L \dots = \sum_l (2l + 1) \dots$. The k -average is defined as $\langle \dots \rangle = (2/N) \sum_{\mathbf{k}} \mu(k) \dots$, $(2/N) \sum_{\mathbf{k}} \mu(k) = 1$, $\mu(k) = (2/N) \sum_{\mathbf{k}} n(k_1)n(k_2)$, where $k_{1,2} = |\frac{1}{2}\mathbf{K} \pm \mathbf{k}|$. Note $(2/N) \sum_{\mathbf{k}} \dots = \int_0^\infty d(k^3) \dots$. Thus, $3k^2\mu(k)$ is the probability of finding two electron momenta \mathbf{k}_1 and \mathbf{k}_2 with the half difference k . Because of

$$\begin{aligned} \rho \int d^3r \left[g_{\pm}^{\text{HF}}(r) - \frac{1}{2} \right] &= \pm(1 - c), \\ \rho \int d^3r \left[g_{\pm}(r) - \frac{1}{2} \right] &= \pm 1, \end{aligned} \quad (6)$$

the corresponding cumulant PDs $h_{\pm}(r) = g_{\pm}^{\text{HF}} - g_{\pm}(r)$ are normalized as

$$\rho \int d^3r h_{\pm}(r) = \mp c. \quad (7)$$

$g_{\pm}(r)$ and $g_{\pm}^{\text{HF}}(r)$ approach $1/2$ for $r \rightarrow \infty$, thus $h_{\pm}(\infty) = 0$. Note $g(r) = [g_+(r) + 3g_-(r)]/2$.

No correlation (corresponding to $r_s = 0$) means $n(k) \rightarrow n^{(0)}(k) = \Theta(1 - k)$, thus $\mu(k) \rightarrow \mu^{(0)}(k) = 4(1 - k)^2(2 + k)\Theta(1 - k)$, cf. Ref.¹⁵, and $h_{\pm}(r) = 0$. In this ideal case the identities

$$\begin{aligned} \sum_L^{\pm} j_l^2(kr) &= \frac{1}{2} \left(1 \pm \frac{\sin 2kr}{2kr} \right), \\ < \frac{\sin 2kr}{2kr} > &= \left(\frac{3j_1(r)}{r} \right)^2, \\ \rho \int d^3r \left(\frac{3j_1(r)}{r} \right)^2 &= 2 \end{aligned} \quad (8)$$

ensure the hole normalizations (1) to be obeyed.

Correlation (corresponding to $r_s \neq 0$) means $n(k) \neq \Theta(1 - k)$ and $h(r) \neq 0$. Recently the HEG-PDs for this case have been successfully parametrized in terms of Overhauser geminals (= 2-body wave functions) $R_l(r, k)$ ⁹⁻¹³, namely as

$$g_{\pm}(r) = \sum_L^{\pm} < R_l^2(r, k) >. \quad (9)$$

So the normalization (7) can be written as

$$\rho \int d^3r \sum_L^{\pm} < [R_l^2(r, k) - j_l^2(kr)] > = \pm c \quad (10)$$

The question arises whether the lhs can be expressed in terms of quantities characterizing the differences between the Overhauser geminals $R_l(r, k)$ (for interacting electrons) and the Bessel functions $j_l(kr)$ (= Overhauser geminals for noninteracting electrons). Here it is shown that these characteristic quantities are the phase shifts $\eta_l(k)$, which describe the large- r asymptotics of the Overhauser geminals $R_l(r, k)$ according to

$$R_l(r, k) \rightarrow \frac{1}{kr} \sin \left(kr - l\frac{\pi}{2} + \eta_l(k) \right) \quad \text{for } r \rightarrow \infty. \quad (11)$$

Namely, within the Overhauser approach a pair of electrons with momenta \underline{k}_1 and \underline{k}_2 moving in the HEG is considered. Their center-of-mass motion is described by $\exp(i\mathbf{K}\mathbf{R})$, where $\mathbf{K} = \underline{k}_1 + \underline{k}_2$ is the total momentum and $\mathbf{R} = (\underline{r}_1 + \underline{r}_2)/2$ is the center-of-mass coordinate. Their relative motion is described by $R_L(\underline{r}, k) = R_l(r, k)Y_L(\underline{e}_r)$ with the relative coordinate $\underline{r} = \underline{r}_1 - \underline{r}_2$ and the half momenta difference $k = \frac{1}{2}|\underline{k}_1 - \underline{k}_2|$. So the total 2-body wave function describing the pair is $\exp(i\mathbf{K}\mathbf{R})R_L(\underline{r}, k)$. The $R_l(r, k)$ are the solutions of the radial Schrödinger equation for the relative motion

$$\left[-\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{r^2} + v_{\text{eff}}^{\pm}(r) - k^2 \right] R_l(r, k) = 0 \quad (12)$$

with $v_{\text{eff}}^{\pm}(r) = \frac{\alpha r_s}{r} + \dots$ as an effective interaction potential. The dots indicate the potential of the physically plausible screening cloud around each electron (resulting from exchange and correlation), possibly different for "+" (even l) and "-" (odd l). Note that Eq. (12) is the remainder of an effective 2-body Schrödinger equation and that $R_l(r, k)$ is (part of) a 2-body wave function, a so-called geminal. Because the effective interaction potential $v_{\text{eff}}^{\pm}(r)$ is repulsive, the solutions of Eq. (12) are scattering states, characterized by the aforementioned scattering phase shifts $\eta_l(k)$. Therefore the integrals $\int d^3r j_l^2(kr)$ and $\int d^3r R_l^2(r, k)$ do not exist, but (the following proof is analog to that in Ref.²¹) understanding the lhs's of Eq. (9) as $\int d^3r \dots = \lim_{R \rightarrow \infty} \int_{r < R} d^3r \dots$ and using the identity

$$\frac{\partial}{\partial \underline{r}} \frac{1}{2} \left(\frac{\partial R_L^*}{\partial \underline{r}} \frac{\partial R_L}{\partial(k^2)} - R_L^* \frac{\partial^2 R_L}{\partial \underline{r} \partial(k^2)} + \text{c.c.} \right) = R_L^* R_L \quad (13)$$

(this follows from Eq. (12)) and the Gauss theorem

$$\int_{r < R} d^3r \frac{\partial}{\partial \underline{r}} [\underline{e}_r f(r)] = 4\pi R^2 f(R), \quad (14)$$

it turns out

$$\int_{r < R} d^3r [R_l^2(r, k) - j_l^2(kr)] = \quad (15)$$

$$\frac{4\pi R^2}{2k} \left(\frac{\partial R_l}{\partial r} \frac{\partial R_l}{\partial k} - R_l \frac{\partial^2 R_l}{\partial r \partial k} - \frac{j_l}{\partial r} \frac{\partial j_l}{\partial k} + j_l \frac{\partial^2 j_l}{\partial r \partial k} \right)_{r=R}.$$

The rhs gives with Eq. (11) the sum $A_l(k) + B_l(k)$, where

$$A_l(k) = \frac{2\pi}{k^2} \eta_l'(k), \quad (16)$$

$$B_l(k) = -\frac{\pi}{k^3} [\sin(2kR - l\pi + 2\eta_l(k)) - \sin(2kR - l\pi)].$$

These expressions have to be k -averaged (with $\mu(k)$) and L -summed. $\mu(k)$ has the properties $\mu(0) = 8(1 - c)$, $\mu(\infty) = 0$, $\mu'(k) < 0$. The discontinuity of $n(k)$ at $k = 1$ (quasiparticle weight z_F) makes $\mu''(k)$ also discontinuous at $k = 1$ and the correlation tail $n(k > 1) \neq 0$ causes a corresponding correlation tail $\mu(k > 1) \neq 0$. The phase shifts are gauged as $\eta_l(\infty) = 0$. Because they originate from a repulsive potential, it is $\eta_l(0) = 0$. (For an attractive potential the Levinson theorem would say $\eta_l(0) = n\pi$ with n = number of bound states in the l -channel, c.f. e.g. Ref.¹⁷ or¹⁸, p. 133.) In addition to this, for repulsive potentials $v_{\text{eff}}^{\pm}(r)$ with finite range it holds $\eta_l(k) \sim k^{2l+1}$. The k -average $< \dots >$ of $A_l(k)$ yields after partial integration

$$< A_l(k) > = 6\pi \int_0^{\infty} dk [-\mu'(k)] \eta_l(k). \quad (17)$$

The other term gives $\langle B_l(k) \rangle_1 + \langle B_l(k) \rangle_2$ with

$$\begin{aligned}\langle B_l(k) \rangle_1 &= - \int_0^\infty dk b_1(k) \sin(2kR - l\pi), \\ b_1(k) &= \frac{3\pi}{k} \mu(k) [\cos 2\eta_l(k) - 1], \\ \langle B_l(k) \rangle_2 &= - \int_0^\infty dk b_2(k) \cos(2kR - l\pi), \\ b_2(k) &= \frac{3\pi}{k} \mu(k) \sin 2\eta_l(k).\end{aligned}\quad (18)$$

Successive partial integrations yield (semi-convergent) series starting with

$$\begin{aligned}\langle B_l(k) \rangle_1 &= - \frac{1}{(2R)^3} [b_1''(1^-) - b_1''(1^+)] \cos(2R - l\pi) \\ &\quad + \frac{1}{(2R)^3} b_1''(0) \cos l\pi + \dots, \\ \langle B_l(k) \rangle_2 &= + \frac{1}{(2R)^2} b_2'(0) \cos l\pi + \dots,\end{aligned}\quad (19)$$

which vanish for $R \rightarrow \infty$. So the 2-body phase-shift sum rules

$$\frac{2}{\pi} \sum_L^\pm \int_0^\infty dk [-\mu'(k)] \eta_l(k) = \pm c \quad (20)$$

follow. These new sum rules are conditions for the effective interaction potential $v_{\text{eff}}^\pm(r)$, which generates the Overhauser geminals $R_l(r, k)$. Whether the phase shifts of the available Overhauser geminals⁹⁻¹² really obey the sum rules (20) has to be checked. For $r_s = 0$ (no correlation) the Löwdin parameter c and the Overhauser phase shifts $\eta_l(k)$ vanish.

The new sum rules (20) are relations between the one-body momentum distribution $n(k)$ encoded in $\mu(k)$ and c and the asymptotic behavior of the PD for large r as described by the phase shifts $\eta_l(k)$ of the Overhauser two-body wave functions $R_l(r, k)$. This may be considered as complementary to the large- k asymptotics of $n(k)$, which is determined by the on-top PD according to $n(k \rightarrow \infty) \sim g_{\uparrow\downarrow}(0)/k^8 + O(1/k^{10})$.^{23,24} A qualitative discussion of the mutual relation between $n(k)$ and $g(r)$ based on the virial theorem is in Ref.²⁵

Note, that the Overhauser geminals result from a 2-body Schrödinger equation with a local effective interaction potential $v_{\text{eff}}^\pm(r)$, whereas the ‘true’ geminals, namely

the natural geminals, which parametrize/diagonalize the 2-body reduced density matrix, are presumably the solutions of a 2-body Schrödinger equation with a non-local effective interaction potential, similarly as the natural orbitals, which diagonalize the 1-body reduced density matrix, follow from an 1-body Schrödinger equation with a non-local effective 1-body potential.

Whereas Eq. (20) is valid for a 2-body quantity of a uniform system (namely the HEG-PDs parametrized by scattering-state Overhauser geminals), the well-known Friedel sum rule for point defects in metals refer to a 1-body quantity of a non-uniform system (namely the charge distribution or screening cloud around the impurity). This cloud perfectly screens the impurity (in a spatially oscillatory manner - Friedel oscillations). The resulting impurity potential generates scattering states with phase shifts $\eta_l(k)$, such that the 1-body sum rule

$$\frac{2}{\pi} \sum_L \eta_l(k_F) = \Delta Z \quad (21)$$

holds. The lhs is the excess charge or the valence difference between the impurity and the host and the rhs is the total number of electronic states induced by the impurity. For the details of this subject cf. e.g. Refs.¹⁸, p. 167, 469 or¹⁹, p. 44. For the generalisation of the Friedel sum rule to non-spherically symmetric scatterers cf.²⁰. For the Sugiyama-Langreth neutrality sum rule of half-space jellium and its generalisation cf.²¹ and²², respectively.

Note the essential difference between Eq. (21), where an external charge causes a perturbation, and Eq. (20), where the ‘blue’ electron, which distorts its surrounding, is an internal charge belonging to the quantum many-body system with the consequences of (i) exchange (singlet/triplet or \pm symmetry) and (ii) of the k average $\langle \dots \rangle$.

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